

EXHAUST GAS PURIFYING CATALYST

Field of the Invention

[0001] The present invention relates to an exhaust gas purifying catalyst, and more particularly to an exhaust gas purifying catalyst that is capable of executing both an NOx absorbing function and a three-way function.

Background of the Invention

[0002] A lean combustion type engine such as a lean burn engine and a direct injection type engine is operated at a leaner air-fuel ratio than a stoichiometrical air-fuel ratio in a predetermined operating range in order to improve the fuel economy characteristics and the exhaust gas characteristics. However a three-way catalyst cannot sufficiently purify NOx in the exhaust gases while the engine is operated at the lean air-fuel ratio. Accordingly, it is known that while the engine is operated at lean air-fuel ratio, nitrogen oxide (NOx) is absorbed from exhaust gases in oxide atmosphere and the absorbed NOx is reduced to nitrogen (N₂) in reduced atmosphere so as to reduce the output of NOx into the air.

[0003] To provide a catalyst with an NOx absorbing function, alkali metals and alkali earth metal, which can be nitrate such as potassium (K) and barium (Ba), are added as an absorbent agent to a catalyst so that the catalyst can function as an NOx absorbent catalyst as disclosed in Japanese laid-open Patent Publication No. 9-85093.

[0004] Fig. 8 shows an NOx purification rate (a value which is measured fifteen seconds after the air-fuel ratio changes to the lean air-fuel ratio) and the total HC (THC) purification rate (a value which is measured at an air-fuel ratio of 30). As is clear from Fig. 8, the NOx absorbing function and the three-way function (the oxidization/reducing function) have a tradeoff relationship. Fig. 9 shows the function expressing a relationship between the NOx purification rate and the THC purification rate after a heat endurance test and the amount of absorbent agent added to a catalyst. During the heat endurance test, a part of the absorbent agent dissipates due to vaporization at a high temperature and the consumption resulting from reaction of the absorbent agent and a cordierite carrier. For this reason, the NOx purification rate after the heat endurance test is lower than that before the heat endurance test, although the THC purification rate after the heat endurance test is higher than that before the heat endurance test. Thus, the NOx purification rate and the THC purification rate have a tradeoff relationship as is the case with Fig. 9. It is therefore difficult for a single catalyst to execute both the NOx absorbing function and the three-way function in a desired manner. Since operation at only the lean air-fuel ratio cannot satisfy a driver's output requirement, a catalyst system needs to execute the three-way function of purifying CO and HC generated during operation at both the stoichiometrical air-fuel ratio and the rich air-fuel ratio. The three-way function is also required for reducing NOx, which is absorbed during the operation at the lean air-fuel ratio. Thus, in order to assure the three-way function, it is ordinarily necessary to intentionally inhibit the NOx absorbing function by restricting the amount of added absorbent agent or forming the absorbent agent by a material having a low absorbent capability. Therefore, a single catalyst cannot satisfactorily execute both the NOx absorbing function and the three-way function. To execute both functions in a desired manner, it is necessary to separately provide an NOx catalyst, which

1 is specialized in absorbing NOx (to which a sufficient amount of absorbent agent is added), and a
2 normal three-way catalyst.

3 4 Summary Of The Invention

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6 [0005] It is therefore an object of the present invention to provide an exhaust gas
7 purifying catalyst that is configured as a single catalyst and is able to execute both an NOx
8 absorbing function and a three-way function in a desired manner.

9 [0006] To attain the above object, the present invention provides an exhaust gas
10 purifying catalyst which includes a carrier, an NOx absorbent catalyst layer and a three-way
11 catalyst layer, and in which at least one absorbent agent selected from a group of alkali metals
12 and alkali earth metals is added to the NOx absorbent catalyst layer, the exhaust gas purifying
13 catalyst wherein: an effect inhibiting material for inhibiting an effect of the absorbent agent on
14 the three-way catalyst is added to at least one of the NOx absorbent catalyst layer and the three-
15 way catalyst. The absorbent agent, which reaches the three-way catalyst, disturbs the CO and
16 HC absorption onto the noble metal of the three-way catalyst due to its electron donating
17 property and moves on a noble metal active surface to cover the surface. The effect inhibiting
18 material inhibits such adverse effects. Consequently, the NOx absorbent catalyst layer and the
19 three-way catalyst layer can be formed on one carrier to thereby form a single catalyst that is
20 able to execute the NOx absorbing function and the three-way function by the NOx absorbent
21 catalyst layer and the three-way catalyst layer, respectively.

Brief Description Of The Drawings

[0007] The invention will now be described with reference to certain embodiments thereof and the accompanying drawings, in which like reference characters designate the same or similar parts throughout the figures and wherein:

Fig. 1 is a local enlarged sectional view showing a quarter of one cell that is formed in an exhaust gas purifying catalyst according to the first embodiment;

Fig. 2 is an explanation drawing showing the affinity of acid material to potassium;

Fig. 3 is a conceptual drawing showing a potassium fixing operation carried out by a cation exchange ability of zeolite;

Fig. 4 is an explanation drawing showing the purification rates of NO_x and THC with respect to the air-fuel ratio;

Fig. 5 is a local enlarged sectional view showing a quarter of one cell that is formed in an exhaust gas purifying catalyst according to the second embodiment;

Fig. 6 is a local enlarged sectional view showing a quarter of one cell that is formed in an exhaust gas purifying catalyst according to the third embodiment;

Fig. 7 is a local enlarged sectional view showing a quarter of one cell that is formed in an exhaust gas purifying catalyst according to the fourth embodiment;

Fig. 8 an explanation drawing showing the purification rates of NO_x and THC with respect to the quantity of added absorbent agent during preparation of a catalyst;

Fig. 9 is an explanation drawing showing the purification rates of NO_x and THC with respect to the quantity of added absorbent agent after heat is endured; and

Fig. 10 is a local enlarged sectional view showing a quarter of one cell formed in an exhaust gas purifying catalyst according to the fifth embodiment.

Detailed Description Of The Invention

[First Embodiment]

[0008] There will now be described an exhaust gas purifying catalyst according to the first embodiment of the present invention with reference to the accompanying drawings.

[0009] The exhaust gas purifying catalyst according to the present embodiment is configured as a catalyst having a honeycomb (monolith) cordierite carrier that is comprised of many cells. Fig. 1 shows a quarter of one cell that is formed in the exhaust gas purifying catalyst according to the present embodiment. For example, a cell of the cordierite carrier 10 has a square shape. For example, the cordierite carrier 10 is produced by mixing alumina powders, silica powders and magnesia powders in such a manner that the ratio of alumina, silica and magnesia can be equal to a cordierite composition, then dispersing the mixture into the water, forming a solid content thereof into a honeycomb form, and sintering the honeycomb compact.

[0010] An absorbent catalyst layer 20 composing an NOx absorbent catalyst layer is formed on the surface of the cordierite carrier 10, and an absorbent agent block layer 30 is formed on the surface of the absorbent catalyst layer 20. A three-way catalyst layer 40 is formed on the surface of the absorbent agent block layer 30. As described hereinbelow, the absorbent catalyst layer 20 mainly executes an NOx absorbing function, the three-way catalyst layer 40 mainly executes a three-way function, the absorbent agent block layer 30 mainly functions as an inhibiting layer that inhibits the movement of an absorbent agent in the absorbent catalyst layer

20 to the three-way catalyst layer 40.

[0011] For example, the absorbent catalyst layer 20 is formed in the following manner. First, a slurry is prepared that includes noble metal such as platinum (Pt); an absorbent agent formed of alkali metal, alkali earth metal, etc. such as potassium (K) and barium (Ba); acid material such as zeolite; and the like. The cordierite carrier 10 is then immersed in the slurry and is sintered after drying. Consequently, acid material 50 is mixed as an effect inhibiting material in the absorbent catalyst layer 20 including the noble metal and the absorbent agent.

[0012] The absorbent agent is typically formed of potassium or barium, but it may be formed of any other materials insofar as they are alkali metals or alkali earth metals. According to the present embodiment, a sufficient amount of absorbent agent is added to the absorbent catalyst layer 20 so as to surely execute a satisfactory NO_x absorbing function according to the characteristics in Fig. 8. The acid material 50 for fixing the absorbent agent is preferably composed of a transition element in the IV group, the V group and the VI group as shown in Fig. 2, or a typical element in the IV group, the V group and the VI group (e.g. Si, P, S, V, Cr, As, Nb, Mo, and W) and has a high affinity with respect to alkali metals or alkali earth metals (Fig. 2 shows the affinity with respect to, e.g. potassium). In view of the reactivity with the absorbent agent, the acid material 50 is preferably composed of silicon (Si) or tungsten (W) that does not disturb the reaction of NO_x and the absorbent agent in the case where the absorbent agent is composed of potassium.

[0013] In particular, the acid material 50 preferably includes at least one of zeolite and titanium dioxide (TiO₂). For example, the zeolite as a complex oxide has an excellent capability to fix an absorbent agent (potassium in this embodiment) by its cation exchange ability. The absorbent agent, which moves within the absorbent catalyst layer 20, may be ionized in high-

1 temperature water moisture. As shown in the conceptual diagram of Fig. 3, the cation exchange
2 ability of the zeolite is in reverse proportion to a ratio of SiO_2 to AlO_2 , and the heat-resisting
3 property of the zeolite is in proportion to this ratio. More specifically, if the ratio of SiO_2 to
4 AlO_2 is small, the absorbent agent fixing property can be intensified because acid points increase
5 with the increase in the quantity of alumina. The small ratio of SiO_2 to AlO_2 also causes
6 decomposition of alumina with a low heat-resisting property and thus deteriorates the heat-
7 resisting property of the acid material 50 itself. Accordingly, the ratio is preferably determined
8 according to the absorbent agent fixing action and the heat-resisting property. The acid material
9 50 may be either a natural product or a synthetic product, but it may preferably have a large
10 specific surface area so as to assure a large physical absorption area.

11 [0014] On the other hand, the absorbent agent block layer 30 is formed on the surface
12 of the absorbent catalyst layer 20, e.g. in the following manner. First, a slurry including zeolite
13 components is prepared, and the cordierite carrier 10 on which the absorbent catalyst layer 20
14 has already been formed is immersed in the slurry. The cordierite carrier 10 is then dried and
15 sintered so that the absorbent agent block layer 30 can be formed on the surface of the absorbent
16 catalyst layer 20.

17 [0015] The absorbent agent block layer 30 formed of zeolite has acid points having the
18 cation exchange ability. As described above with respect to the absorbent catalyst layer 20, the
19 zeolite has an excellent capability to fix the absorbent agent. When the absorbent agent, which
20 moves from the absorbent catalyst layer 20 to the absorbent agent block layer 30 is ionized in
21 high-temperature water moisture, the absorbent agent is fixed as ions by the cation exchange
22 ability of the acid points in the zeolite. The absorbent agent block layer 30 has a three-
23 dimensional reticulated structure and has a large specific surface area. Since the potassium is

highly dispersed on the absorbent agent block layer 30, it cannot easily enter the three-way catalyst layer 40.

[0016] The absorbent agent block layer 30 may be composed of various types of zeolite such as an MFI type, a Y type, an X type, mordenite and ferrierite. The zeolite conforming to the exhaust gas composition is selected in view of the structural relationship between the zeolite and the absorption class HC. As has been described with respect to the absorbent catalyst layer 20, the cation exchange ability of the zeolite is in reverse proportion to a ratio of SiO_2 to AlO_2 , and the heat-resisting property of the zeolite is in proportion to this ratio. Thus, the ratio is preferably determined according to the absorbent agent fixing action and the heat-resisting property.

[0017] On the other hand, the three-way catalyst layer 40 is formed on the surface of the absorbent agent block layer 30 in, e.g. the following manner. First, a slurry is prepared which includes noble metal such as platinum (Pt), palladium (Pd) and rhodium (Rh), and acid materials. The cordierite carrier 10, on which the absorbent catalyst layer 20 and the absorbent agent block layer 30 have already been formed, is immersed in the slurry. The cordierite carrier 10 is then dried and sintered so that the three-way catalyst layer 40 can be formed on the surface of the absorbent agent block layer 30. An acid material 60 as an effect inhibiting material is mixed in the three-way catalyst layer 40. To satisfactory execute the three-way function, no absorbent agent is added to the three-way catalyst layer 40 according to the characteristics in Fig. 8 of the present embodiment.

[0018] The acid material 60 includes a material for reacting with a stable substance by inhibiting a very high electron donating property of the absorbent agent formed of alkali salt. For example, this material is silica (SiO_2) or tungsten (W), and more preferably, phosphorus (P)

that strongly reacts with alkali.

[0019] The absorbent agent such as potassium and barium included in the absorbent catalyst layer 20 of the catalyst that is constructed in the above-mentioned manner is fixed in the absorbent catalyst layer 20 by the cation exchange ability of the acid material 50 such as zeolite. This fixing action prevents the vaporization of the absorbent agent at a high temperature and the reaction consumption resulting from the movement of the absorbent agent to the cordierite carrier 10, and also inhibits the movement of the absorbent agent to the three-way catalyst layer 40.

[0020] The absorbent agent block layer 30 helps to inhibit the movement of the absorbent agent to the three-way catalyst layer 40. Even if the absorbent agent is removed from the absorbent catalyst layer 20, the absorbent agent does not easily reach the three-way catalyst layer 40 because the absorbent agent is fixed as ions in the absorbent agent block layer 30 by the cation exchange ability of the acid point and is highly dispersed in the absorbent agent block layer 30 having a large specific surface area.

[0021] On the other hand, even if the absorbent agent reaches the three-way catalyst layer 40 regardless of the movement inhibiting action by the acid material in the absorbent catalyst layer 20 and the absorbent agent block layer 30, the absorbent agent reacts with the acid material in the three-way catalyst layer 40 and thus transforms into a harmless and stable substance. If, for example, the potassium is added as the absorbent agent to the absorbent catalyst layer 20 and the phosphorus is added as the acid material to the three-way catalyst layer 40, the potassium having moved to the three-way catalyst layer 40 reacts with the phosphorus and transforms into potassium phosphate.

1 [0022] The potassium phosphate is a very stable substance, which has no electron
2 donating property or has no property of moving on a noble metal active surface of the three-way
3 catalyst layer. Thus, even if the absorbent agent moves from the absorbent catalyst layer 20 onto
4 the three-way catalyst layer 40, it is possible to prevent the following adverse effects: the
5 electron donating property of the absorbent agent disturbs the CO and HC absorption onto the
6 noble metal and the absorbent agent moves on the noble metal active surface to cover the
7 surface. Consequently, the absorbent catalyst layer 20 including the absorbent agent and the
8 three-way catalyst layer 40 including no absorbent agent can be formed on the cordierite carrier
9 10 to thereby form a single catalyst.

10 [0023] This catalyst absorbs NO_x as nitrate in exhaust gases emitted from the engine
11 that is operating at the lean air-fuel ratio due to the operation of the absorbent agent dispersed in
12 the absorbent catalyst layer 20. While the engine is operating at the rich air-fuel ratio, the
13 absorbent agent emits nitrate that reacts with CO, etc. on the noble metal of the three-way
14 catalyst layer 40 and is reduced into nitrogen. The nitrogen is then emitted from the catalyst.

15 [0024] The absorbent catalyst layer 20 is capable of satisfactorily executing the NO_x
16 absorbing function since a sufficient amount of absorbent agent is added to it. The three-way
17 catalyst layer 40 is capable of satisfactorily executing the three-way function because no
18 absorbent agent is added. It is therefore possible to prevent the above-mentioned adverse effects
19 of the absorbent agent. The three-way catalyst layer 40 surely purifies NO_x and also purifies CO
20 and HC, which are generated while the engine is operating at the stoichiometrical and rich air-
21 fuel ratios. The exhaust gas purifying catalyst according to the present embodiment is very
22 advantageous because it is configured as a single catalyst that can be manufactured at a low cost
23 and it can execute the NO_x absorbing function and the three-way function in a desired manner.

1 [0025] Fig. 4 shows the purification rates of NOx and THC with respect to the air-fuel
2 ratio. A conventional catalyst indicated by a broken line in Fig. 4 can achieve the preferable
3 NOx purification rate but cannot achieve the satisfactory THC purification rate because the NOx
4 absorbing function is given priority (the amount of added absorbent agent is increased). To the
5 contrary, the catalyst according to the present embodiment can achieve the satisfactory
6 purification rate with respect to the THC as well as NOx.

7 [Second Embodiment]

8 [0026] There will now be described an exhaust gas purifying catalyst according to the
9 second embodiment of the present invention.

10 [0027] As shown in Fig. 5, the exhaust gas purifying catalyst in the present
11 embodiment is constructed in the same manner as in the first embodiment except that the
12 absorbent catalyst layer 20 and the three-way catalyst layer 40 are replaced with one another in
13 arrangement.

14 [0028] Thus, the process of manufacturing the exhaust gas purifying catalyst according
15 to the present embodiment comprises a step of forming the three-way catalyst layer 40 including
16 the acid material 60 such as phosphorus on the cordierite carrier 10, a step of forming the
17 absorbent agent block layer 30 formed of zeolite, etc. on the three-way catalyst layer 40, and a
18 step of forming the absorbent catalyst layer 20 including the absorbent agent as alkali salt and the
19 acid material 50 such as zeolite.

20 [0029] In the exhaust gas purifying catalyst according to the present embodiment that is
21 constructed in the above-mentioned manner, the acid material 50 in the absorbent catalyst layer
22 20 and the absorbent agent block layer 30 inhibit the movement of the absorbent agent in the
23 absorbent catalyst layer 20 to the three-way catalyst layer 40, and the absorbent agent having

1 reached the three-way catalyst is transformed into a stable substance by the acid material 60 as is
2 the case with the first embodiment. Thus, the absorbent agent has no adverse effect on the three-
3 way catalyst layer 40. Therefore, the absorbent catalyst layer 20 including the absorbent agent
4 and the three-way catalyst layer 40 including no absorbent agent can be formed on one carrier 10
5 to thereby form a single catalyst, which that can be manufactured at a low cost and execute the
6 NOx absorbing function and the three-way function in a desired manner.

7 [Third Embodiment]

8 [0030] There will now be described an exhaust gas purifying catalyst according to the
9 third embodiment of the present invention.

10 [0031] As shown in Fig. 6, the exhaust gas purifying catalyst of the present
11 embodiment has the same structure as that of the first embodiment except that the absorbent
12 agent block layer 30 is omitted. Thus, the process of manufacturing the exhaust gas purifying
13 catalyst of the present embodiment comprises a step of forming the absorbent catalyst layer 20
14 including the absorbent agent as alkali salt and the acid material 50 such as zeolite on the carrier
15 10 and a step of forming the three-way catalyst layer 40 including the acid material such as
16 phosphorus.

17 [0032] The exhaust gas purifying catalyst that is constructed in the above-mentioned
18 manner cannot achieve the absorbent agent movement inhibiting operation by the absorbent
19 agent block layer 30 as has been described with regard to the first embodiment. However, the
20 absorbent agent is fixed by the acid material 50 in the absorbent catalyst layer 20, and the acid
21 material 60 in the three-way catalyst layer 40 transforms the absorbent agent into a stable
22 substance. Therefore, the absorbent agent has no adverse effect on the three-way catalyst layer
23 40. Therefore, the absorbent catalyst layer 20 including the absorbent agent and the three-way

1 catalyst layer 40 including no absorbent agent can be formed on one carrier 10 to thereby form a
2 single catalyst, which can be manufactured at a low cost and execute the NOx absorbing function
3 and the three-way function in a desired manner.

4 [Fourth Embodiment]

5 [0033] There will now be described an exhaust gas purifying catalyst according to the
6 fourth embodiment of the present invention.

7 [0034] As shown in Fig. 7, the exhaust gas purifying catalyst of the present
8 embodiment has the same structure as that of the first embodiment except that the acid material
9 60 is omitted from the three-way catalyst layer 40.

10 [0035] Thus, the process of manufacturing the exhaust gas purifying catalyst of the
11 present embodiment comprises a step of forming the absorbent catalyst layer 20 including the
12 absorbent agent as alkali salt and the acid material 50 such as zeolite on the carrier 10 and a step
13 of forming the three-way catalyst layer 40. Unlike the first embodiment, a slurry in which no
14 acid material 60 such as phosphorus is mixed is used for forming the three-way catalyst layer 40.

15 [0036] The exhaust gas purifying catalyst that is constructed in the above-mentioned
16 manner cannot execute the absorbent agent movement inhibiting operation by the absorbent
17 agent block layer 30 as has been described with regard to the first embodiment; however, the
18 acid material 50 in the absorbent catalyst layer 20 and the absorbent agent block layer 30 inhibit
19 the movement of the absorbent agent in the absorbent catalyst layer 20 to the three-way catalyst
20 layer 40. Thus, the absorbent agent has no adverse effect on the three-way catalyst layer 40.
21 Therefore, the absorbent catalyst layer 20 including the absorbent agent and the three-way
22 catalyst layer 40 including no absorbent agent can be formed on one carrier 10 to thereby form a
23 single catalyst, which can be manufactured at a low cost and execute both the NOx absorbing

function and the three-way function in a desired manner.

[Fifth Embodiment]

[0037] There will now be described an exhaust gas purifying catalyst according to the fifth embodiment of the present invention.

[0038] As shown in Fig. 10, the exhaust gas purifying catalyst of the present embodiment has the same structure as that of the first embodiment except that the effect inhibiting materials (the acid materials 50, 60) is not added to the absorbent catalyst layer 20 and the three-way catalyst layer 40.

Thus, the process of manufacturing the exhaust gas purifying catalyst of the present embodiment comprises a step of forming the absorbent catalyst layer 20 including the absorbent agent as alkali salt, a step of forming the absorbent agent block layer 30 formed of zeolite on the absorbent catalyst layer 20, and a step of forming the three-way catalyst layer 40. Unlike the first embodiment, a slurry to which the acid materials 50, 60 are not added is mixed is used for forming the absorbent catalyst layer 20 and the three-way catalyst layer 40.

[0039] The exhaust gas purifying catalyst that is constructed in the above-mentioned manner cannot achieve the operation by the acid materials 50, 60 in the absorbent catalyst layer 20 and the three-way catalyst layer as has been described with regard to the first embodiment; however, the absorbent agent block layer 30 inhibit the movement of the absorbent agent in the absorbent catalyst layer 20 to the three-way catalyst layer 40. Thus, the absorbent agent has no adverse effect on the three-way catalyst layer 40. Even if the effect inhibiting materials such as the acid materials 50, 60 are not added to the absorbent catalyst layer 20 or the three-way catalyst layer 40, the absorbent agent block layer 30 is able to achieve an absorbent agent movement inhibiting effect to thereby sufficiently inhibit the effect of the absorbent agent on the three-way

1 catalyst layer 40. For example, the absorbent agent block layer 30 has an effect inhibiting layer,
2 to which an effect inhibiting material for inhibiting the effect of the absorbent agent on the three-
3 way catalyst layer is added. The catalyst of the present embodiment is formed as a single
4 catalyst by forming the absorbent catalyst layer 20 and the three-way catalyst layer 40 on the
5 carrier. Moreover, the catalyst of the present embodiment is able to satisfactorily execute both
6 the NOx absorbing function and the three-way function and has a great deal of flexibility when
7 being assembled into an exhaust system.

8 [0040] It should be understood, however, that there is no intention to limit the invention
9 to the first through fifth embodiments disclosed, but on the contrary, the invention is to cover all
10 modifications, alternate constructions and equivalents falling within the spirit and scope of the
11 invention as expressed in the appended claims. For example, the acid material 50 may be
12 omitted from the absorbent catalyst layer 20 in the first embodiment, and the acid material 50
13 may be omitted from the absorbent catalyst layer 20 or the acid material 60 may be omitted from
14 the three-way catalyst layer 40, respectively; and the acid material 50 may be omitted from the
15 absorbent catalyst layer 20 or the acid material 60 may be omitted from the three-way catalyst
16 layer 40 in the third embodiment. Further, the absorbent catalyst layer 20 and the three-way
17 catalyst layer 40 may be replaced with each other in arrangement, and the three-way catalyst
18 layer 40 may be formed between the carrier 10 and the absorbent agent block layer 30 and the
19 absorbent catalyst layer 20 may be formed on the surface of the absorbent agent block layer 30.
20 Further, the absorbent agent block layer 30 may be replaced with an effect inhibiting layer to
21 which an effect inhibiting material for inhibiting the effect of the absorbent agent on the three-
22 way catalyst layer 40 is added.

1 [0041] According to the above-mentioned embodiments, the honeycomb cordierite
2 carrier 10 is used as the carrier, but the present invention may also be applied to an exhaust gas
3 purifying catalyst having a carrier that is made of other material than cordierite. For example,
4 the same operational effects can be achieved by using a metal carrier. Further, if the honeycomb
5 cordierite carrier is used, the cells of the cordierite carrier should not necessarily be square but
6 may also be triangle or hexagonal.